3 µm water vapor self- and foreign-continuum: New method for determination and new insights into the self-continuum

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Determination of H2O continua in the past

Method

- Transmittance spectra from FTS, absorption coefficients from CRDS
- Calculation of H2O local lines using mostly HITRAN parameters
- Only use troughs, subtract local line contributions

Disadvantages (especially for FC)

- Large gaps
- Low resolution
- Errors due to inadequacy of line parameter database

New method for H2O continuum determination

Method

- Usage of same spectra for line parameter and continuum determination
- Continuum extracted from fitted baseline from microwindow-based multispectrum fit

Advantage

- Continuum information not constrained to troughs – only few gaps
- Local line errors small
- Sufficient spectral resolution – determined by microwindow width, baseline = polynomial, degree ≤ 2
- Advantage is largest for in-band FC

Prototyping

- Water measurements between 1800 and 4000 cm-1 with high quality line parameters already determined [Loos2017;Loos2017a]

- Since 1990 high resolution spectroscopy for spectroscopic databases of atmospheric constituents
- Commercial Bruker IFS125 HR FT spectrometer 10-40000 cm-1

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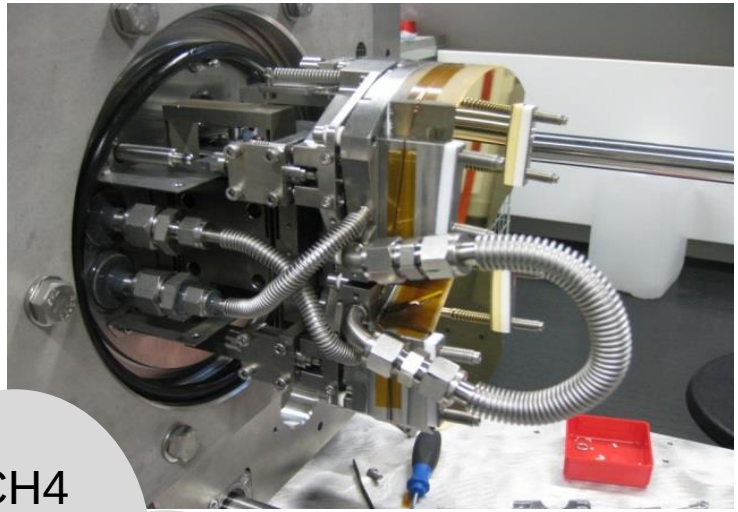
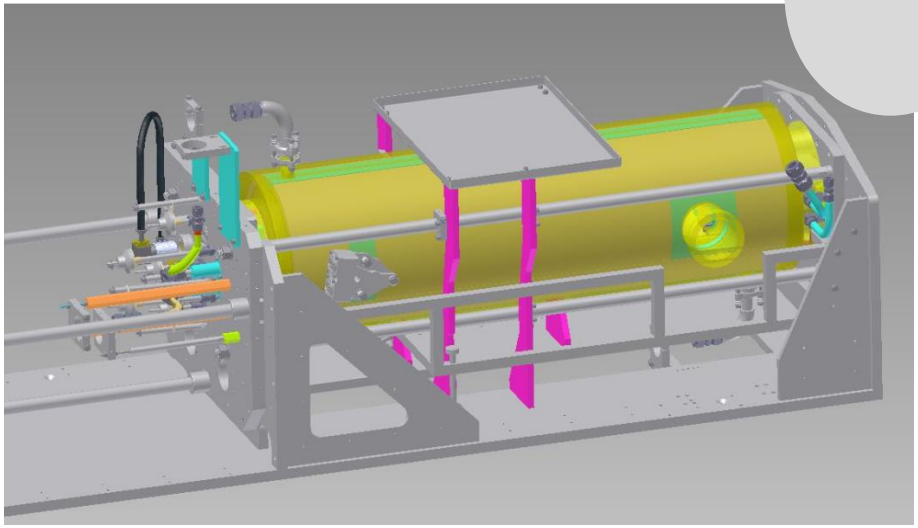
Multireflection cell

- 14-165 m absorption path, accuracy 0.1%
- 190-350 K temperature range
- Mirrors actively thermalized
- 0.1 K temperature homogeneity
- Attached to Bruker IFS 125 HR
- Transfer optics in sample chamber
- Mirror coating selected for minimum reflection loss





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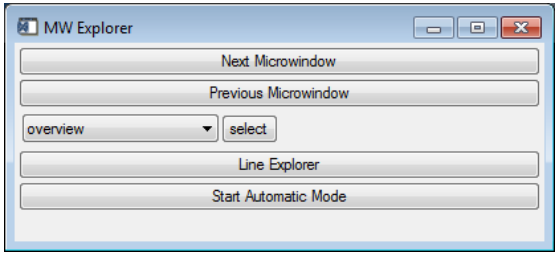
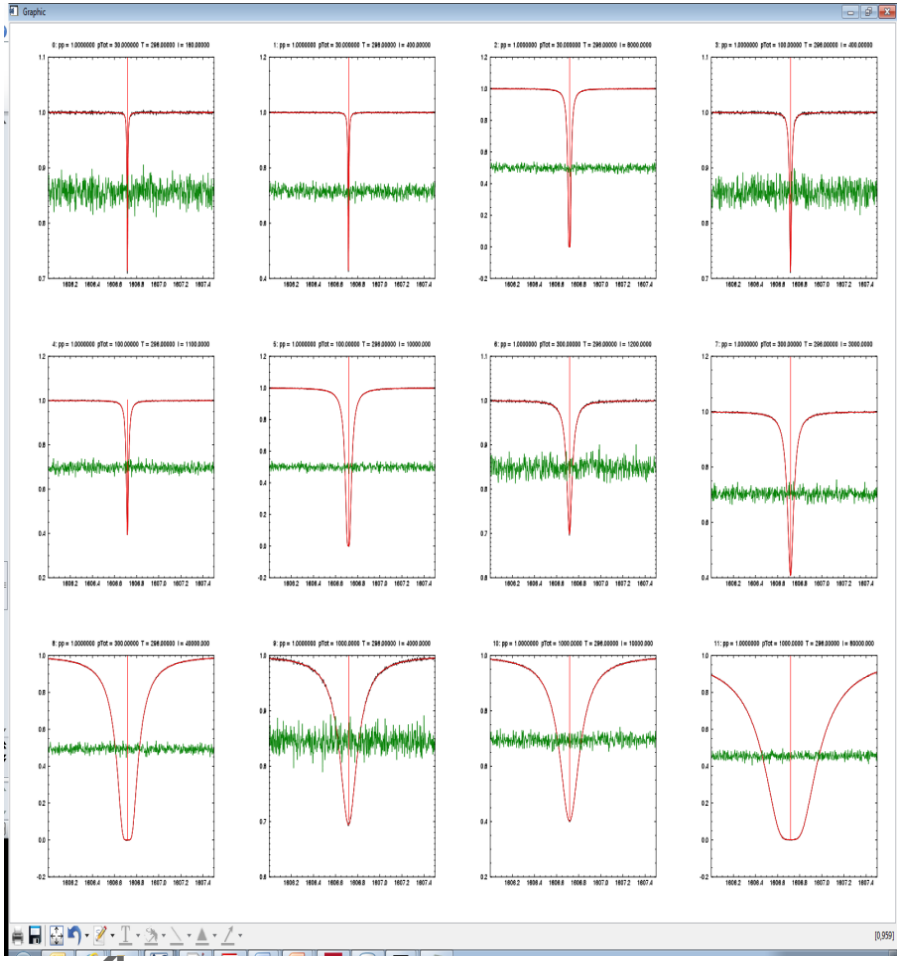
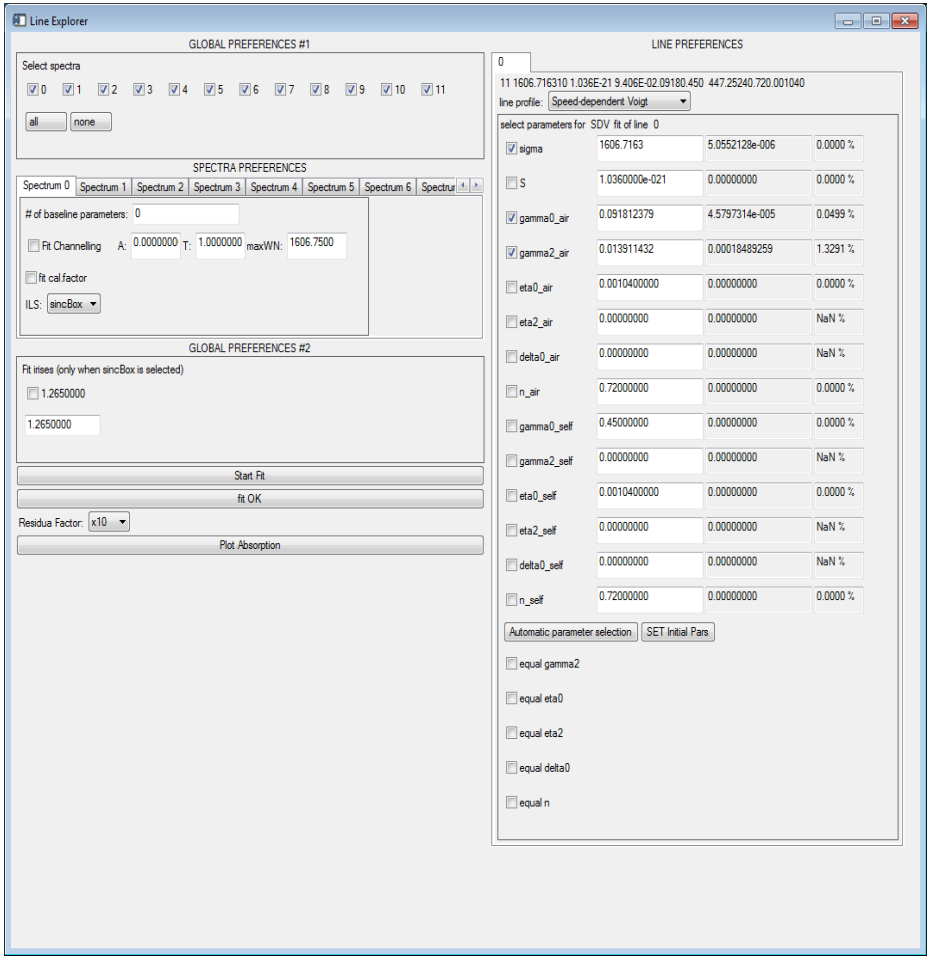
Other infrastructure: Gas handling

- Precision pressure transducers: mks Baratron 0.05% accuracy
- Temperature sensors: Lakeshore Pt100, 0.1 K accuracy
- 800 l stainless steel gas mixing chamber, stirrer
- Flow and pressure controllers

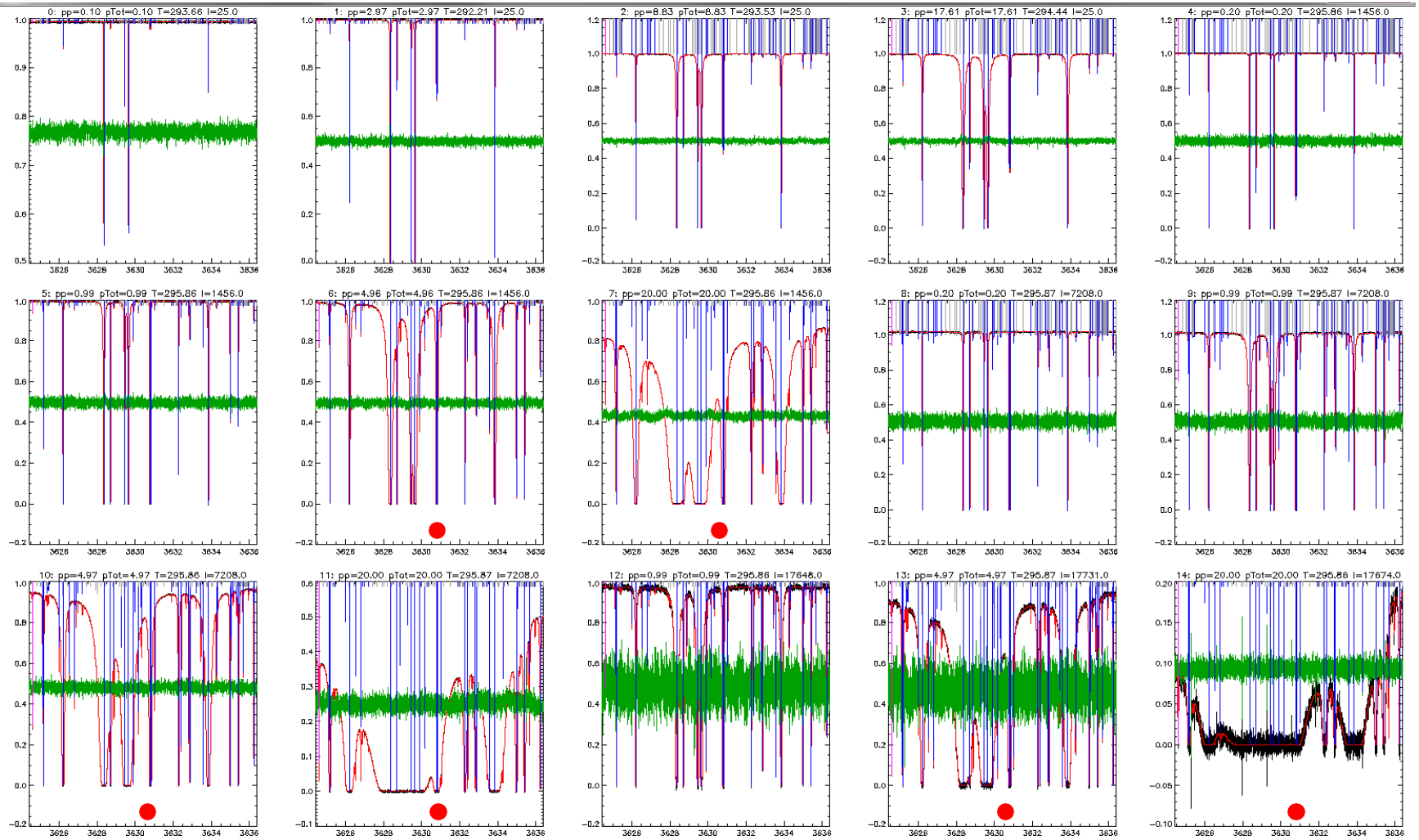
Multispectrum fitting software







Multispectrum fit of pure H2O spectra



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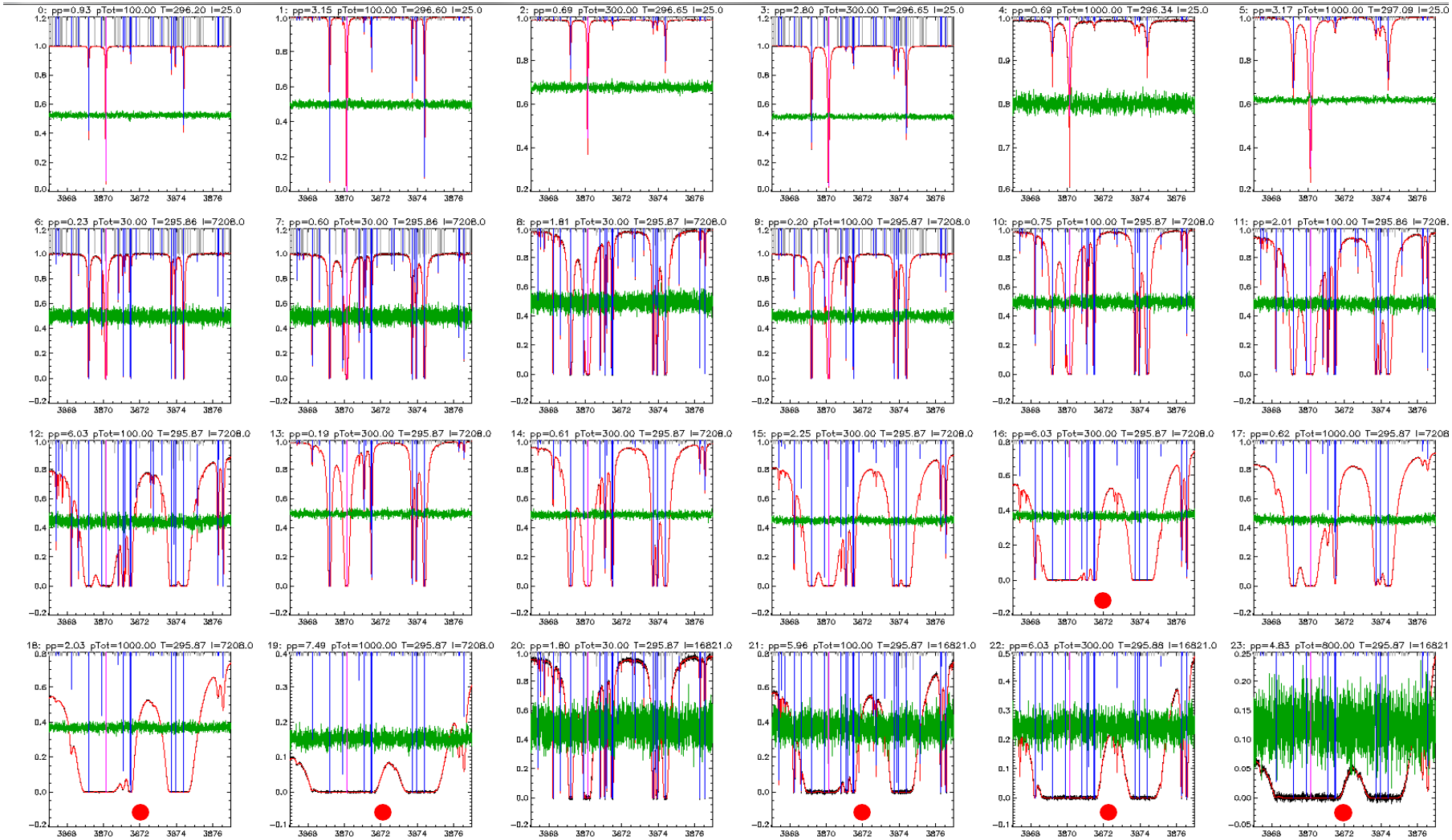
Multispectrum fit of air-broadened H2O spectra



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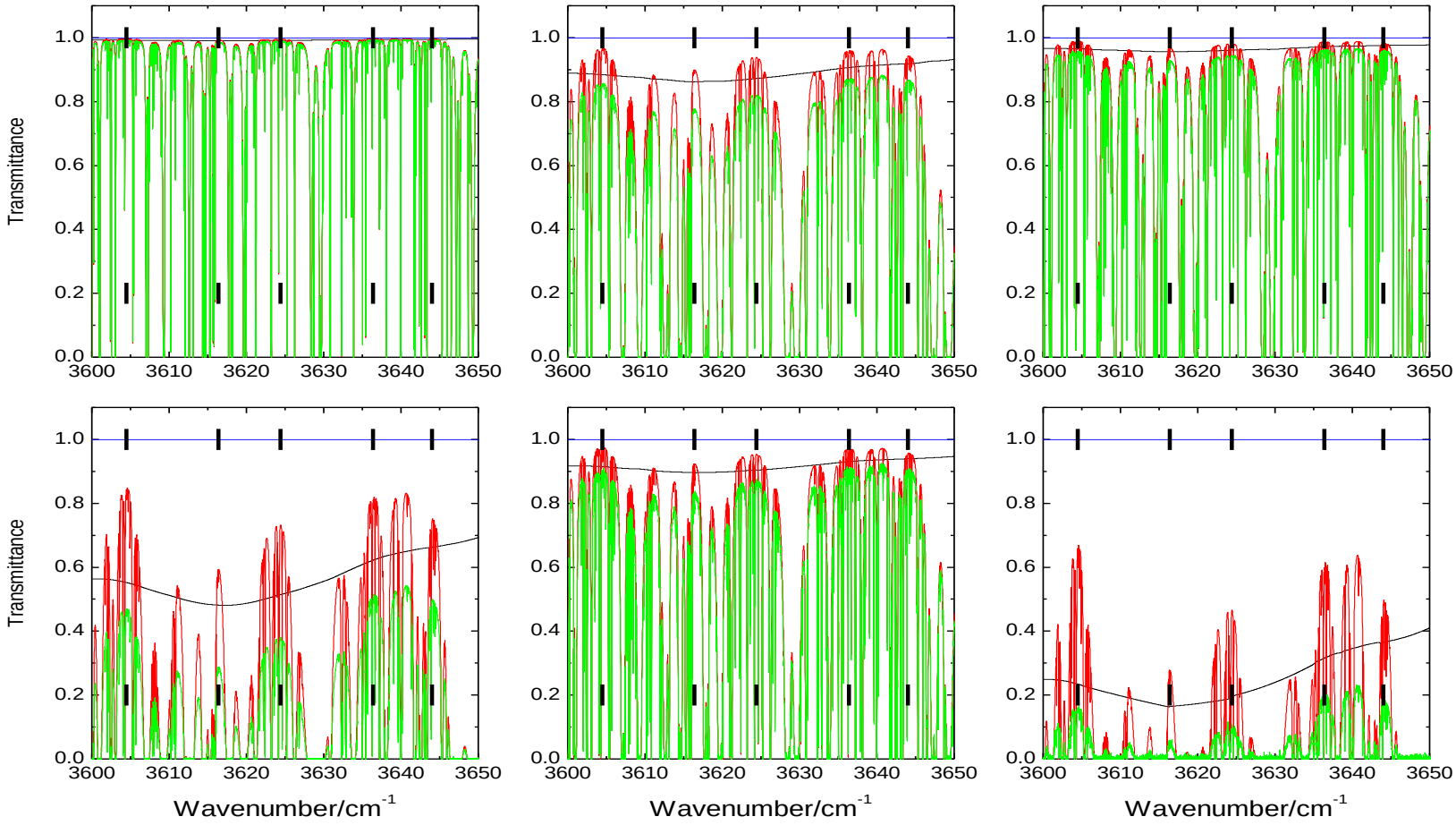
Measurements used for continuum determination

- $SC \propto p_{H2O}^2 \cdot l = IC_s$
- $FC \propto p_{H2O} \cdot p_{air} \cdot l = IC_f$

#	p_{H2O}/mbar	p_{tot}/mbar	l/m	IC_s	IC_f
1	4.9626	4.9626	14.50	350	
2	20.0	20.0	14.50	5800	
3	4.9651	4.9651	72.08	1773	
4	20.0	20.0	72.08	28800	
5	4.9655	4.9655	177.3	4354	
6	20.0	20.0	176.7	70680	
7	6.0	300	72.08	2592	129600
8	2.0	1000	72.08	288	144000
9	7.5	1000	72.08	4050	540000
10	6.0	100	168.21	6048	100800
11	6.0	300	168.21	6048	302400
12	4.8	800	168.21	3870	645000

Transmittance contributions of pure H2O spectra

green: observed, red: pure line spectrum, black: baseline



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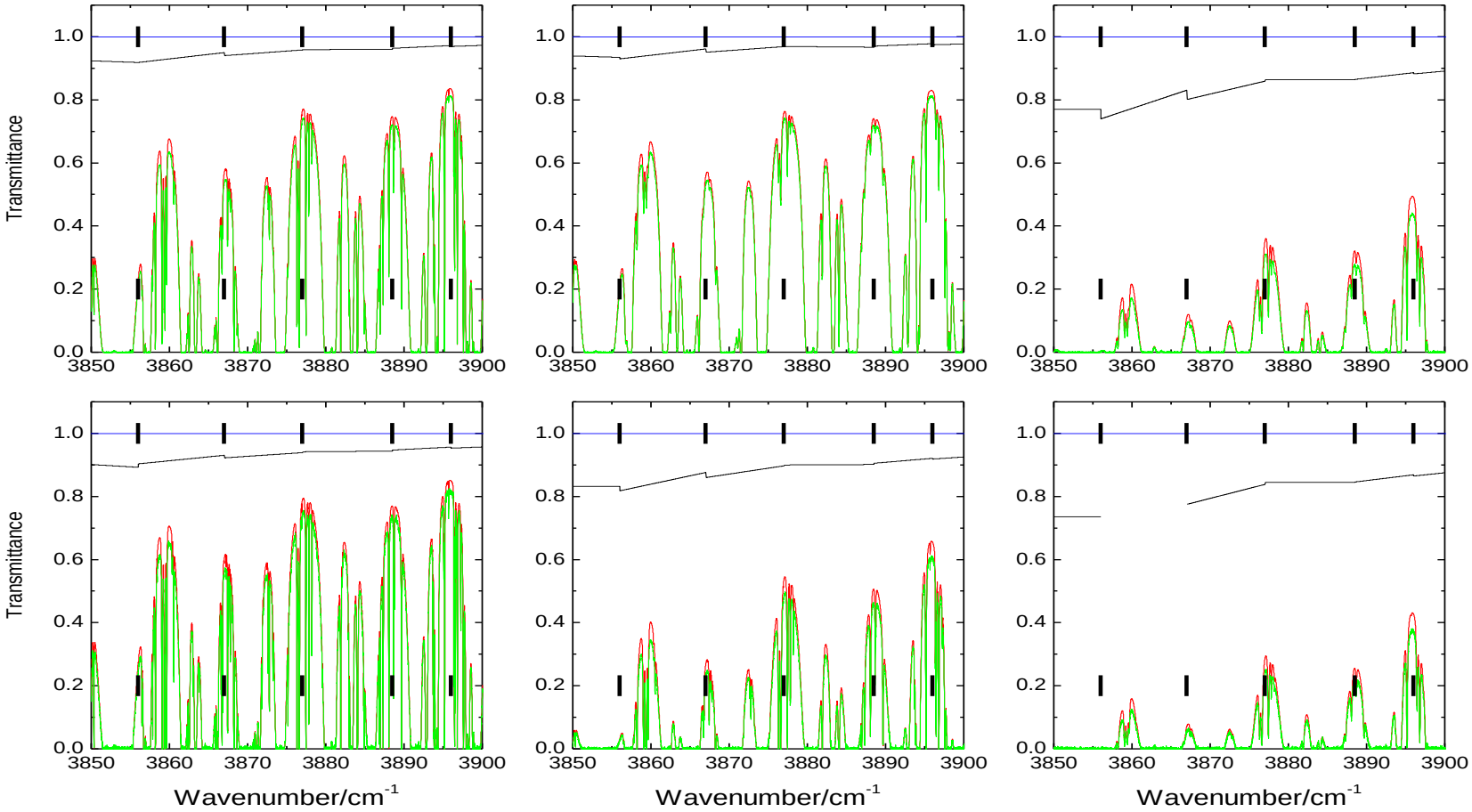
Transmittance contributions of air-broadened H2O spectra

green: observed, red: pure line spectrum, black: baseline



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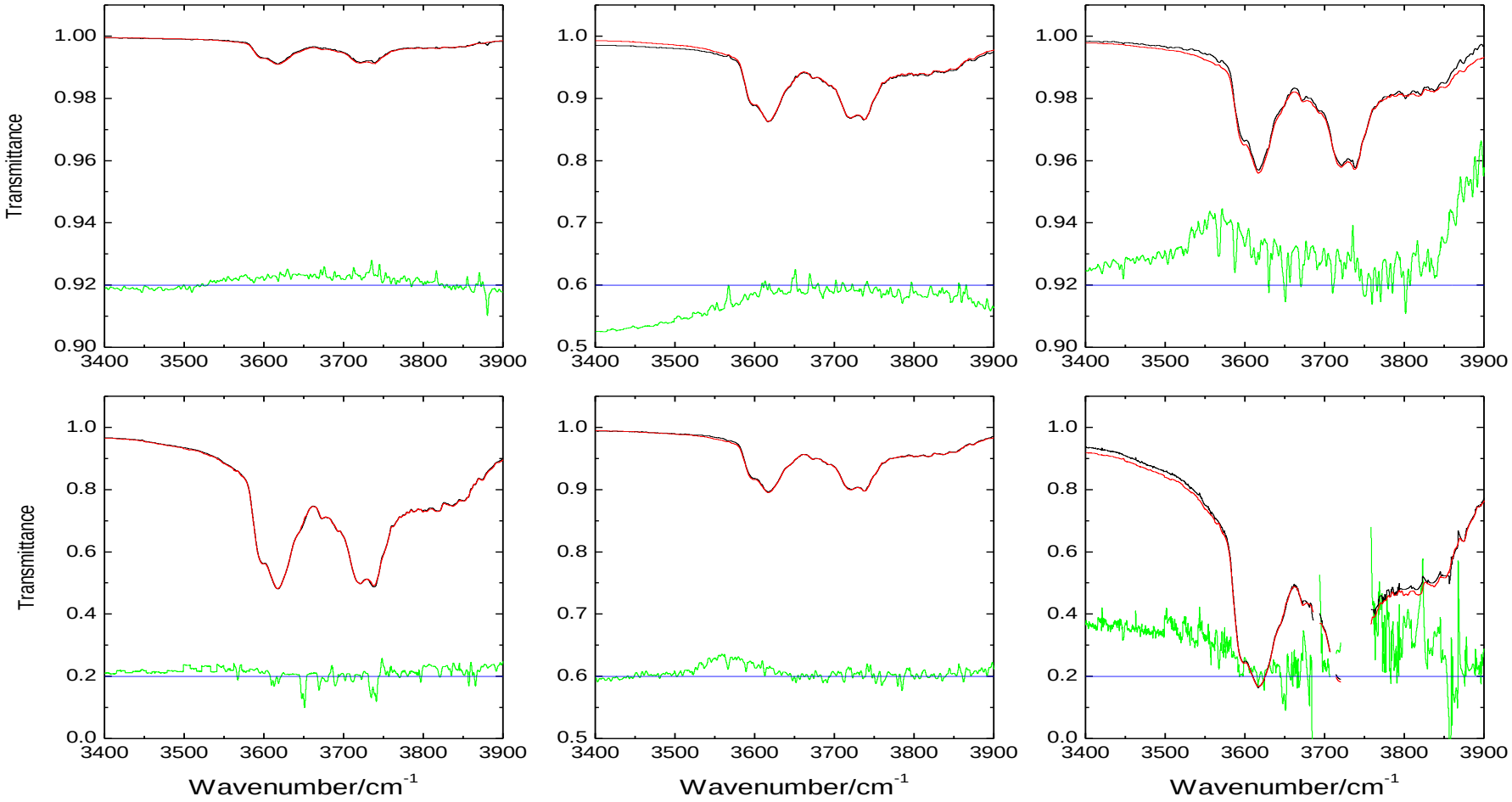
Self-Continuum multispectrum fit to baselines

black: observed, red: calc, green: OMCx10



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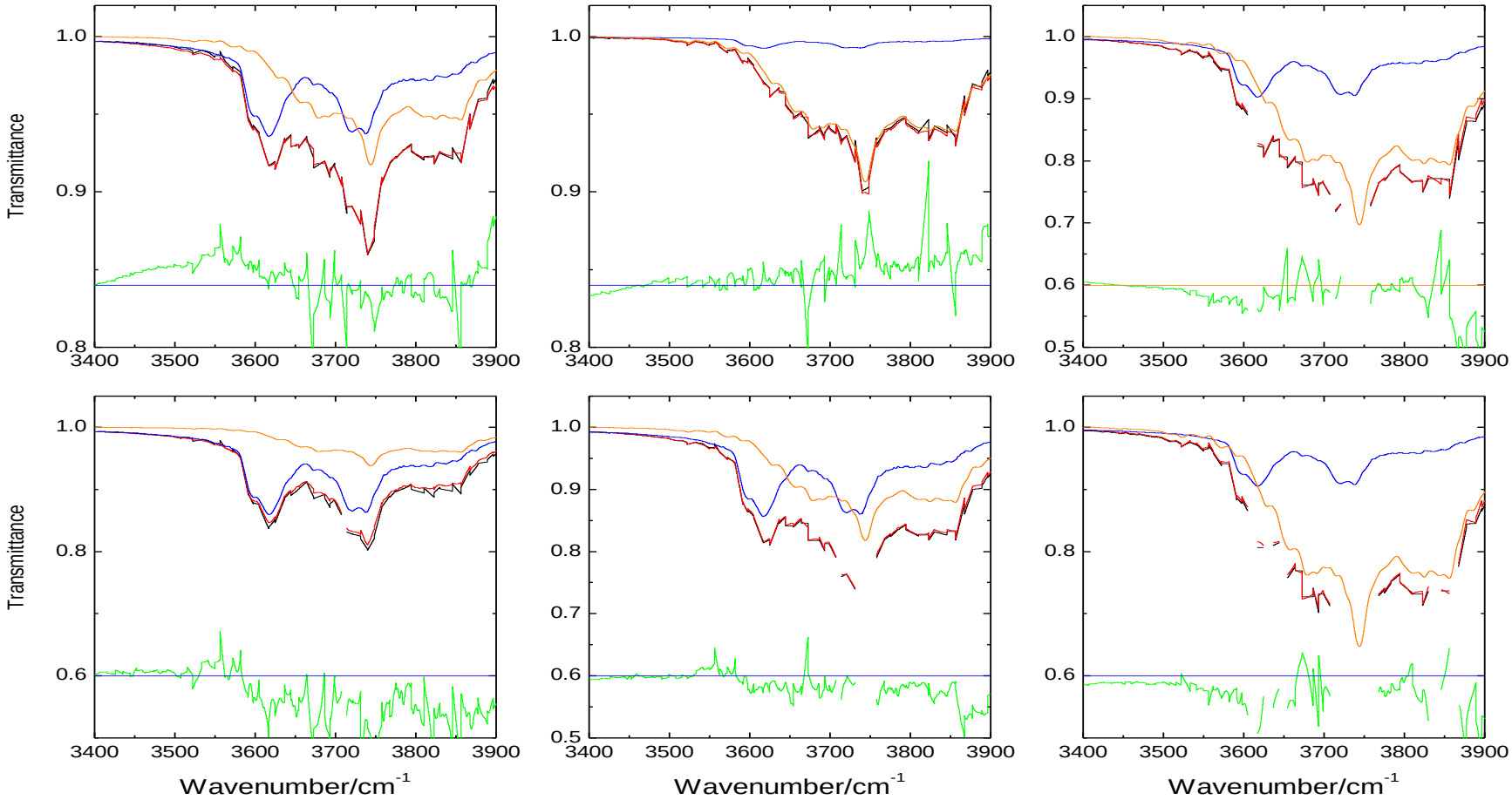
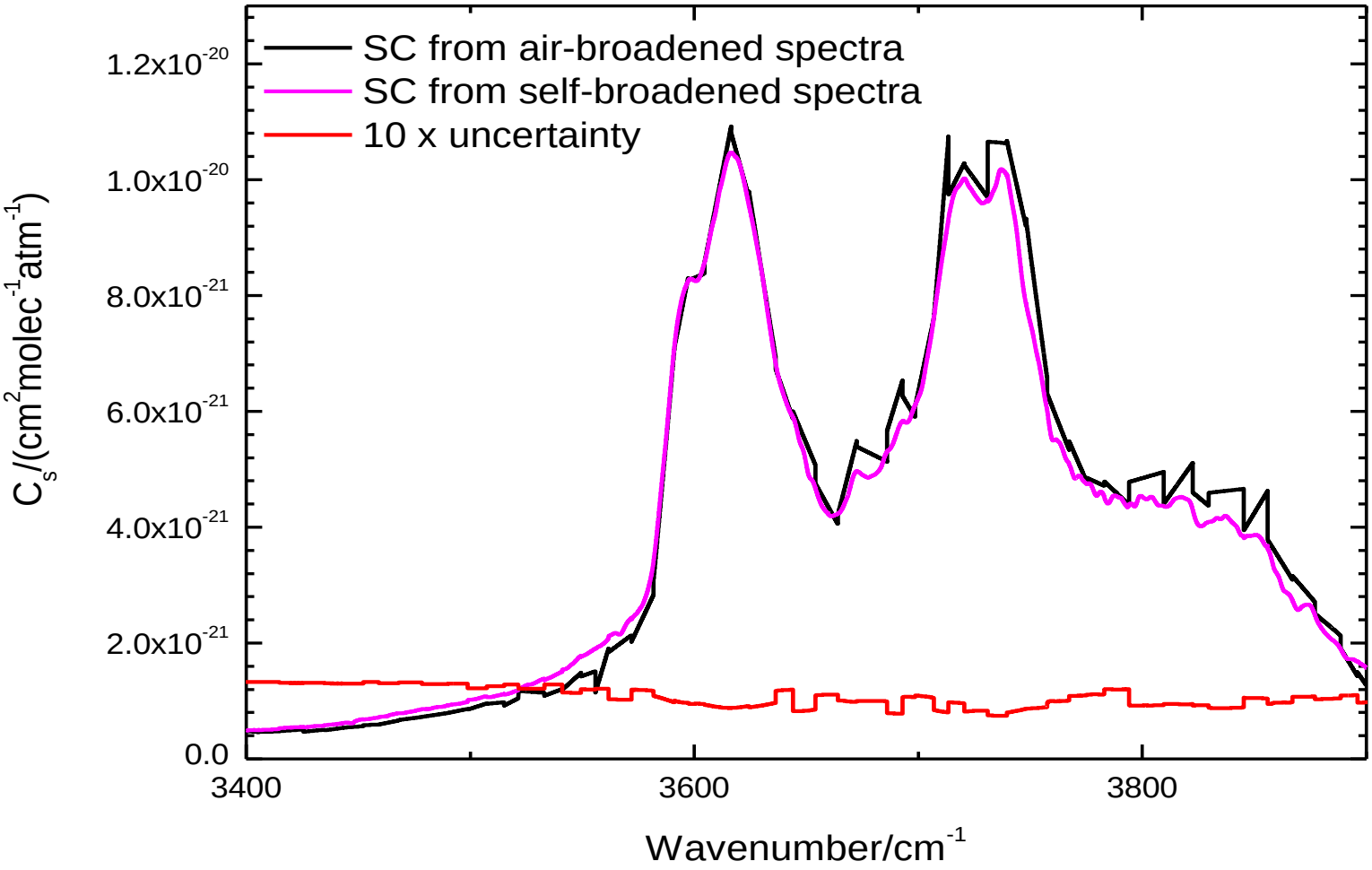
Foreign-Continuum multispectrum fit to baselines

black: observed, red: calc, blue: SC contribution, yellow: FC contribution, green: OMCx10

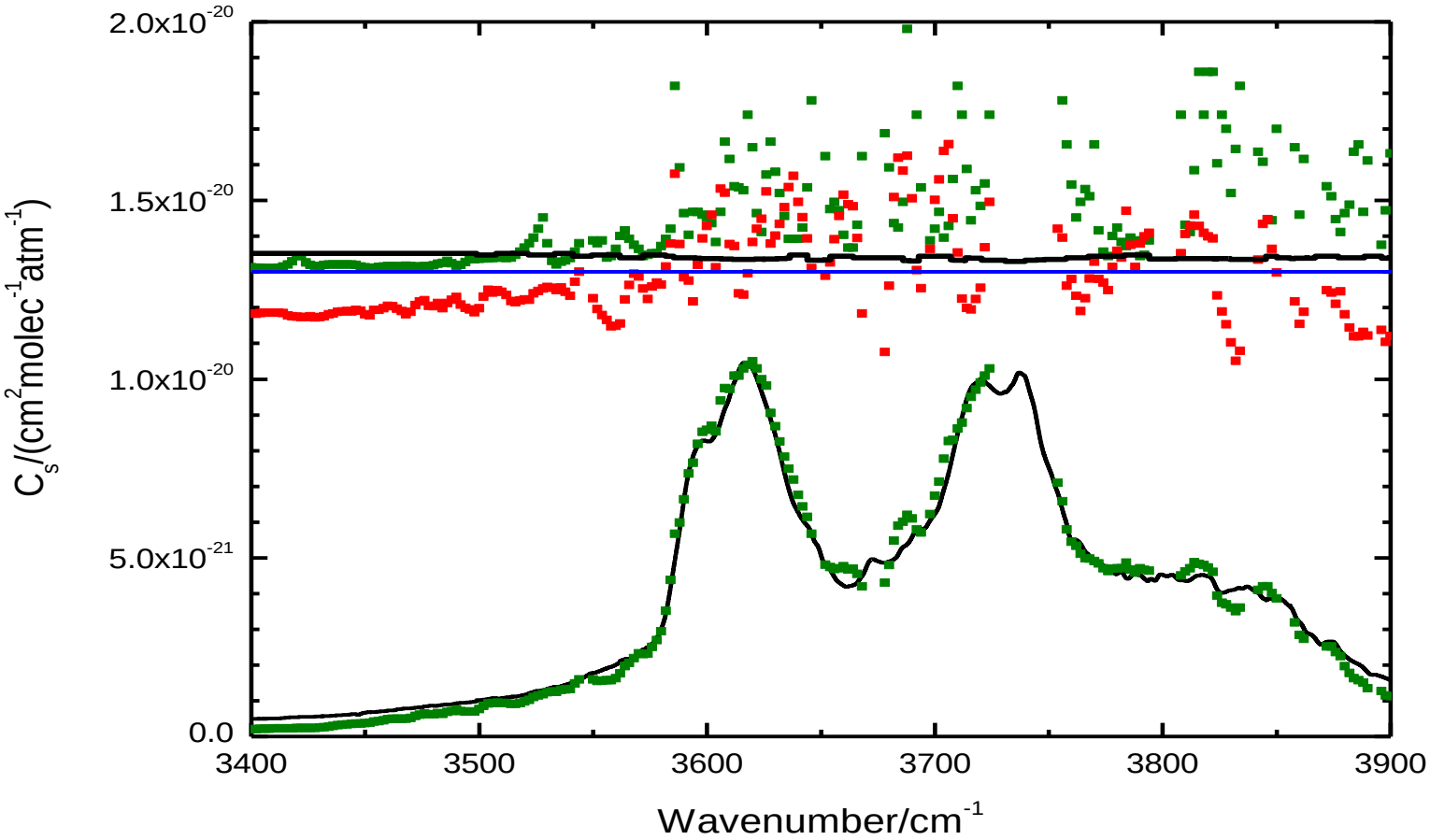


Validation of SC with air-broadened measurements

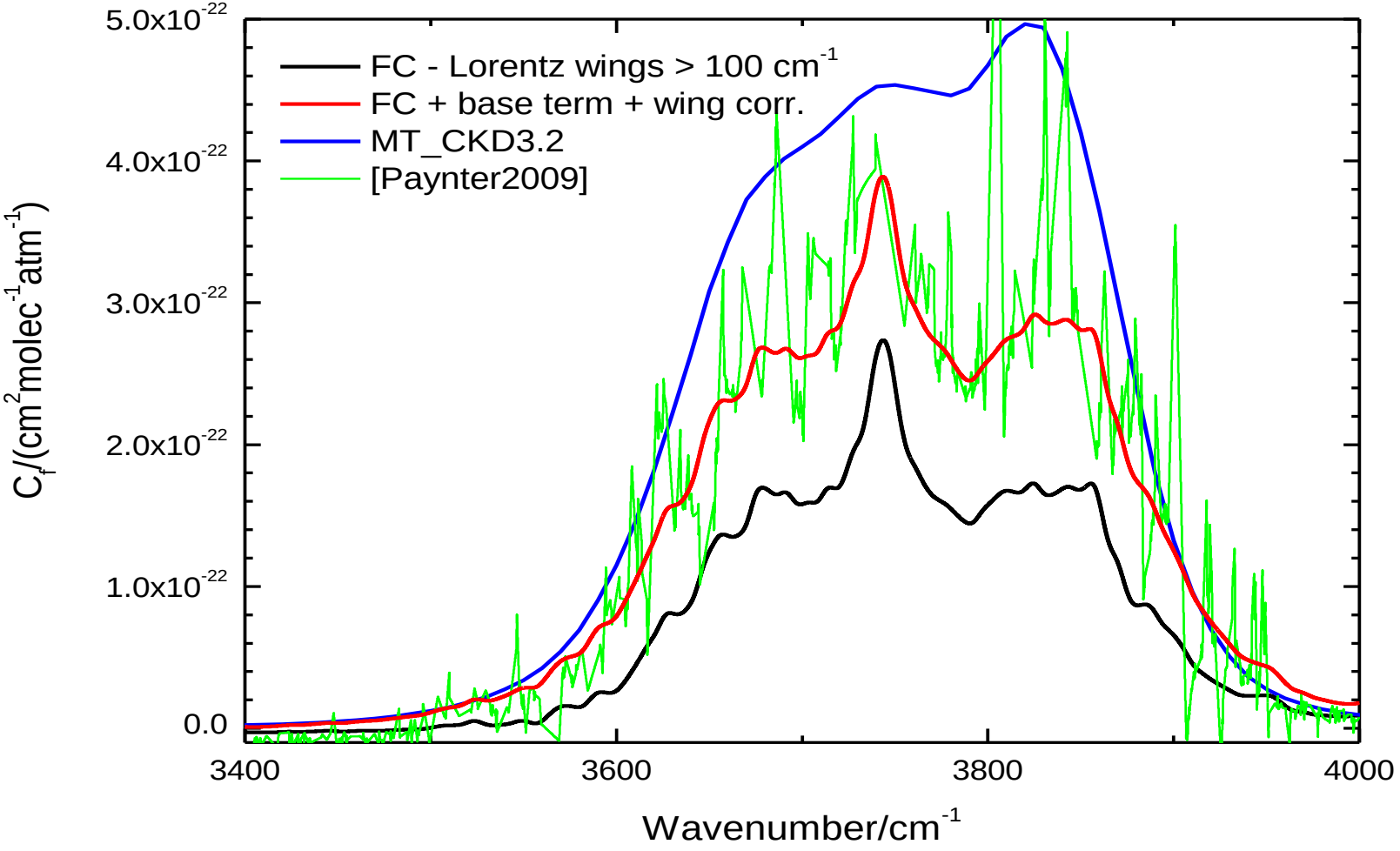


Comparison of SC with CAVIAR

lower traces: continua, upper traces: uncertainties/differences x 4, zero blue line. Black: present work, green: CAVIAR, red: CAVIAR – present work



Comparison of FC with CAVIAR and MT_CKD3.2



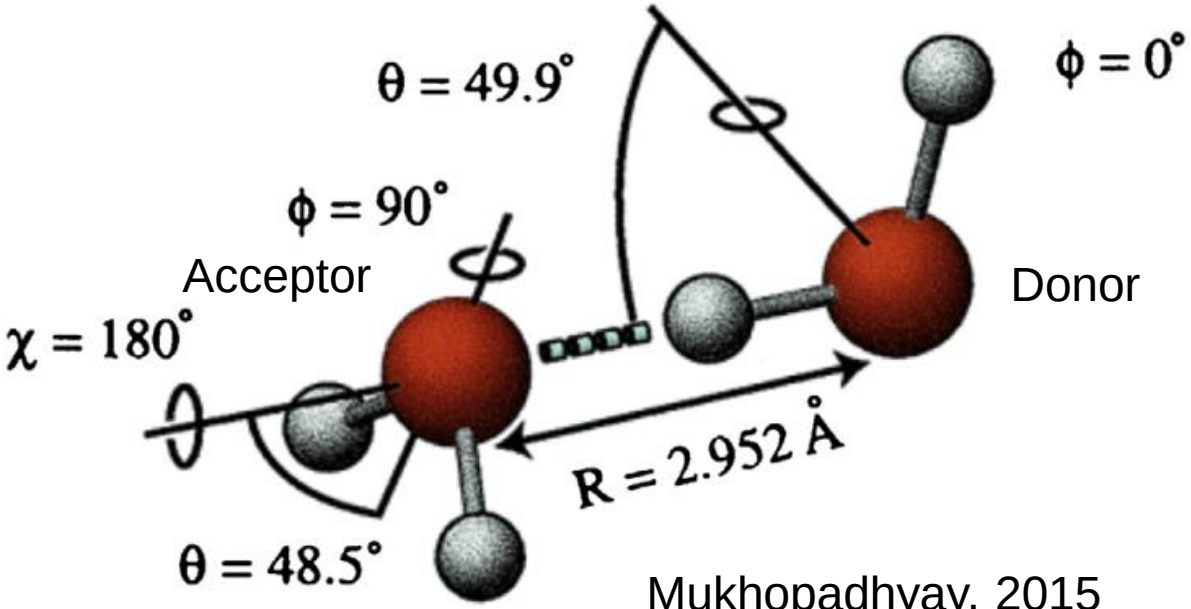
Shape of self-continuum

- H2O-dimer dissociating into monomer
- Spectrum in between bound dimer and monomer
- Ab initio can calculate spectra but high energy level density close to dissociation limit

- Simpler approach: Bound dimer + quasibound dimer
- Quasibound dimer has shape of monomer band but large broadening due to short lifetime (FWHM=14-40 cm-1, Ptashnik, 2011).
- New concept for estimating bound dimer spectrum: Generic band shapes of parallel and perpendicular rovibrational bands

Shape of bound dimer bands

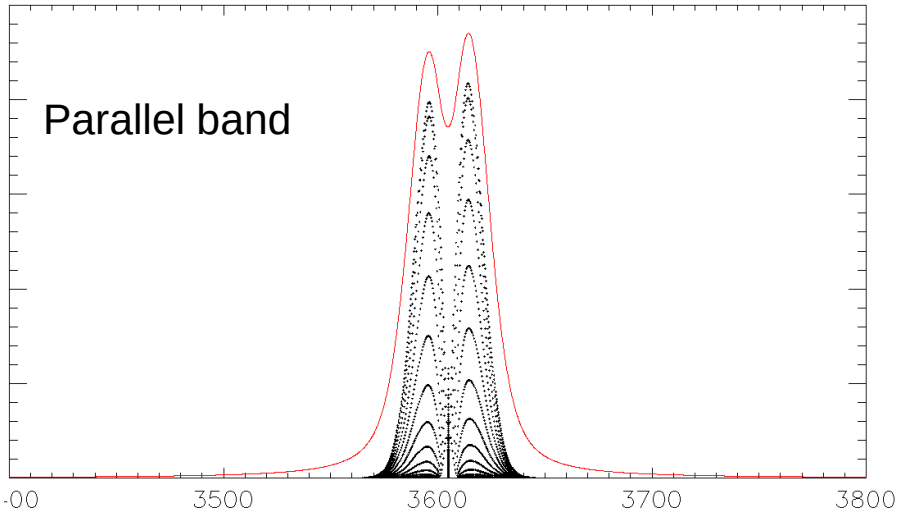
- Strongest vibrational fundamentals in 3 µm region from ab initio/experiments:
  - symmetric OH stretch of the donor H_2O: ν_3
  - antisymmetric OH stretch of the donor H_2O: ν_1
  - antisymmetric OH stretch of the acceptor H_2O: ν_9
- Ground state rotational constants: A ≈ 7 cm^{-1}, B ≈ C ≈ 0.2 cm^{-1}

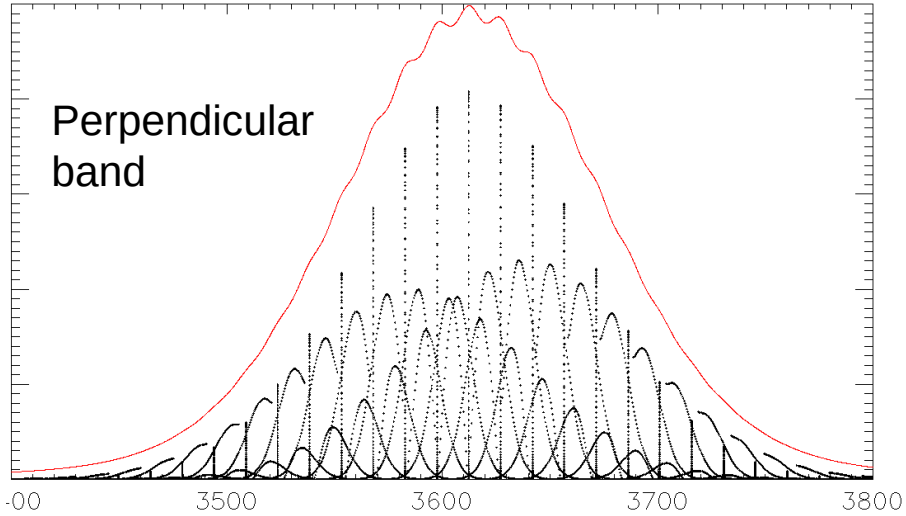


Mukhopadhyay, 2015

Shape of bound dimer bands

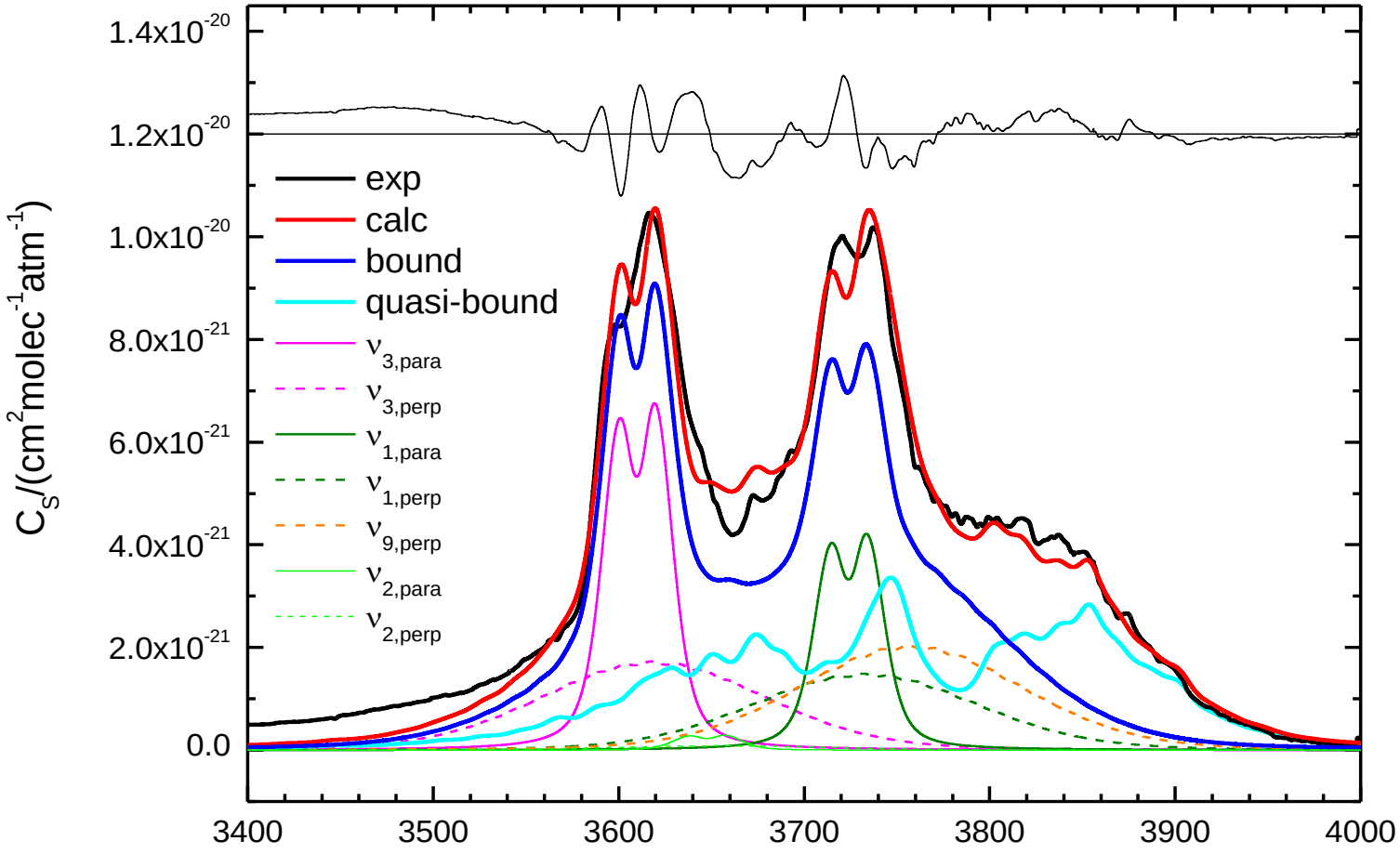
- Ptashnik: All bands have Lorentzian shape with 60 cm^{-1} FWHM
- New approach: Generic band shapes of parallel and perpendicular bands of symmetric top
- ν_3, ν_1: dipole moment changes parallel and perpendicular to A-axis, ν_9: perp.
- Effects smearing band structure: diff. rot. const. in ground and excited vib. states, centrifugal distortion, hot bands (ca. 85% of total intensity), asymmetry splitting, torsional tunneling splitting, lifetime broadening, Cave: floppy molecule
- FWHM parallel band rovibrational lines: 5 cm^{-1}, perpendicular band 10 cm^{-1}





Fit of SC continuum

#	K_{Db} /atm^{-1}	K_{Dq} /atm^{-1}	K_{eq} /atm^{-1}	$fS_{\nu3}$	$fS_{\nu1}$	$fS_{\nu9}$	$fpara_{\nu3}$	$fpara_{\nu1}$	$\nu_{0,\nu3}$ /cm^{-1}	$\nu_{0,\nu1}$ /cm^{-1}	$\nu_{0,\nu9}$ /cm^{-1}	FWHM qD /cm^{-1}
fit	0.025	0.042	0.067	0.48	0.27	0.25	0.54	0.6	3610	3724	3749	20
lit			0.052	0.55(8)	0.28(6)	0.18(3)			3597	3730	3749	



Conclusion

- New method for H2O in-band continuum determination prototyped, using same spectra for line parameters and continuum
- Example: FC and SC in 3 µm region
- Continua show better spectral coverage and resolution, and smoothness
- SC in good agreement with CAVIAR work
- FC in agreement with CAVIAR work, showing P-, Q-, and R-branch
- SC was fitted applying bound and quasibound dimer contributions
- Rovibrational bands of bound dimer were simulated by generic parallel and perpendicular symmetric top bands
- Two double peaks in SC can be modelled with parallel rovibrational bands
- Dimer band positions and strengths are in reasonable agreement with theoretical work